On the CIEEL mechanism of triggerable dioxetanes: Does the electron jump or is it charge transfer?

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1,2-Dioxetanes are of particular value for the chemical generation of excited states, a process known as chemiluminescence, in view of the accompanying light emission. This may be achieved either thermally or by electron transfer; the latter mode is known as chemically initiated electron-exchange luminescence (CIEEL). A prominent and well studied biological prototype of the CIEEL phenomenon is the firefly bioluminescence, in which the light emission is triggered enzymatically. The mechanistic elucidation of this triggering process requires an in-depth understanding of both the dioxetane cleavage and the chemiexcitation process. Computational work supports full electron transfer and reveals the following salient mechanistic features: The electron transfer requires initially the elongation of the O-O bond in the triggered dioxetane and once the electron is transferred, the activation energy for the rupture of the peroxide ring is significantly lowered. Furthermore, for the chemiexcitation step, a concerted cleavage of the dioxetane ring may operate with concomitant excited-state generation through charge transfer (CT) from the electron donor (the phenolate functionality released on triggering) to the electron acceptor (the peroxide bond in the dioxetane). Alternatively, a stepwise process may apply in which initially one-electron transfer to the peroxide bond takes place and causes dioxetane cleavage into a radical-ion pair, followed by excited-state generation through electron back-transfer (BET). The chemiexcitation efficiency depends decisively on the location (meta versus para position) of the triggerable phenolate functionality. A detailed electronic analysis of this triggered light emission is consistent with the BET mechanism. The efficiency of the BET process depends on the distribution of the electrons among the two oxygen atoms of the ring-opened dioxetane to which the electron is transferred from the triggerable functionality, \emph{i.e.}, the unpaired electron may be localized on the oxygen atom proximate to the phenolate functionality or placed onto the remote one. The latter mechanistic alternative is supported by the observed viscosity dependence of the light efficiency, since a solvent-cage effect operates in the CIEEL process.